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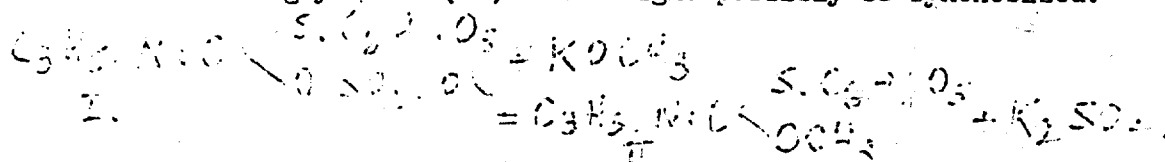
Investigations of mustard oil glycosides. V. The constitution of sinigrin.

by Wilhelm Schneider and Fritz Arede.

Berichte d. Deutschen Chem. Ges. Vol. 47 (1914), pp 2225-2229.

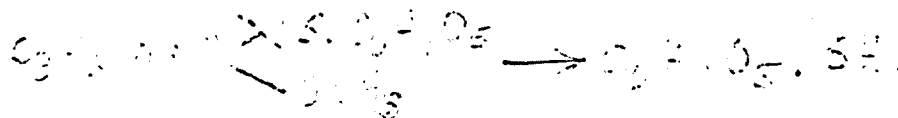
The formula which Gadamer assigned to sinigrin, the mustard oil glycoside from *Brassica nigra*, on the basis of his fine investigations (1) 17 years ago, requires further experimental confirmation in several respects. While this researcher was able to show with probability that the sugar molecule is linked to the sulfur of the mustard oil residue, this linkage so far has not been subjected to strict proof.

For about 2 years one of us (Schneider, 2) has tried to separate the potassium bisulfate residue of sinigrin by means of potassium methylate and to replace it with methoxyl. By this method he hoped to get from sinigrin (I) to a thiourethane-glycoside (II) which might possibly be synthesized:



Since the thiourethane-glycosides aliphatically substituted in connection with nitrogen meanwhile were found (3) to be compounds so decomposable that they cannot be isolated as such, these attempts progressed unsuccessfully at first. The investigation of the decomposition products of these synthetic glycosides, however, had led to the discovery of a highly interesting new sugar compound, thioglucose, $\text{C}_6\text{H}_{11}\text{O}_5$, which had been isolated in the form of its silver salt (4).

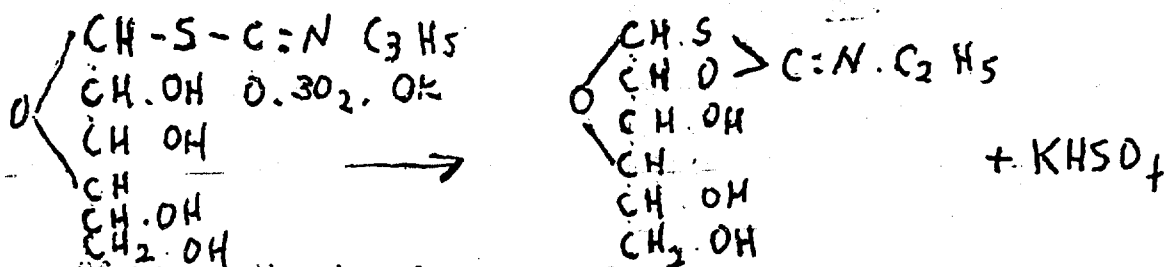
We have now succeeded in obtaining the same silver compound from the resultant product of the reaction of potassium methylate with sinigrin. Thus a strict proof is submitted of the fact that in sinigrin the sugar actually is attached to the sulfur, as required by Gadamer's formula. Potassium methylate therefore really influences sinigrin in the sense of above formulation, at least partly. However, the resulting primary thiourethane-glycoside soon decomposes and forms thioglucose:



The formation of thioglucose from glycoside was also observed upon treatment of a methyl-alcoholic sinigrin solution with ammonia gas.

The influence of potassium methylate is only partly exerted, with intermediate formation of thiourethane glycoside, since a nicely crystallizing compound could be isolated from the reaction product, the composition of which is expressed by the formula $\text{C}_{12}\text{H}_{15}\text{O}_5\text{KS}$, consequently differs from that of sinigrin only by the absence of the potassium bisulfate molecule. We suggest

the name "nerosinigrin" for the new compound. Nerosinigrin rotates the plane of polarized light strongly to the right, consequently still contains the sugar complex of sinigrin, but is extraordinarily stable in contrast to this glycoside. Its sulfur atom is not separated by boiling with alkaline lead solution; nor is it parted by boiling with diluted acids. This fact points to the probability that nerosinigrin has a sulfurous ring complex in its molecule, in whose formation the glucose molecule has a share. Accordingly, nerosinigrin yields a well-defined triacetyl derivative, thus contains only three free glucose-hydroxyls. Quite probably it then has a constitution expressed by formula III, which is easily derived from Gadamer's sinigrin formula according to the scheme:



Of course, the ring closure may also occur by means of the beta-carbinol group of the glucose.

Experimental part.

Influence of potassium methyrate on sinigrin.

Isolation of thioglucose-silver.

6 g crystallized sinigrin (Merck) are dissolved in 100 ccm heated methyl alcohol freshly distilled over sodium. A solution of 0.564 g metallic potassium in 10 ccm absolute methyl alcohol is added to the boiling liquid. Immediately, considerable quantities of potassium sulfate settle out. The reaction fluid is boiled for about one minute more, then it is cooled and separated from potassium sulfate by filtration. The light brown filtrate is heavily concentrated in vacuo; the remaining potassium sulfate is precipitated from the residue by the addition of 500 ccm absolute ethyl alcohol. After repeated filtration an aqueous ammoniacal silver solution prepared from 0.5 g silver nitrate is added. The silver salt of thioglucose immediately settles in light yellow, amorphous flakes which gradually turn brown under the fluid. After settlement, the precipitate is decanted, drawn off by suction and washed with alcohol. The yield of the preparation, dried first over phosphorous pentoxide, then in vacuo at the temperature of chloroform vapor, amounted to 0.45 g. It dissolves easily in cold water; the solution decomposes, however, upon heating and forms silver sulfide and silver mirror. Otherwise thioglucose silver obtained from sinigrin has the same properties as preparations produced by the decomposition of synthetic thiourethane-glycosides. Only its composition differs slightly from that of the others, so far as the silver content was found to be a little too high. This may be due to the circumstance that this time the amorphous salt has adsorbed and carried over an impurity richer in silver, e.g. mustard oil silver sulfate or silver sulfite. Nor was it possible to obtain a preparation with a considerably lower silver content by solution in water and re-precipitation with alcoholic ammonia or by decomposition by means of hydrogen sulfide and reconstitution with ammoniacal

silver solution. Still, the analytical data and the total properties should suffice to prove that the described method will produce the same compound, considered to be the silver salt of thioglucose, from sinigrin.

0.2639 g substance: 0.2270 g CO₂, 0.0844 g H₂O.

0.1709 g substance: 0.0050 g AgCl, 0.1271 g BaSO₄.

C₁₀H₁₁O₅S.g. Calculated: C 23.76, H 3.66, S 10.58, Ag 35.59
Found: C 23.03, H 3.63, S 10.22, Ag 37.43.

In addition, after treatment of a methyl alcoholic sinigrin solution with dry ammonia gas for 24 hours at room temperature, the formation of thioglucose could be demonstrated qualitatively with ammoniacal silver solution.

Merosingrin, C₁₀H₁₅O₅NS.

The alcoholic reaction liquid obtained by the influence of potassium methylate on sinigrin and freed of resultant thioglucose by the method described above, yields an additional degradation product of sinigrin in a side reaction. The filtrate of thioglucose silver is freed of excessive silver by the addition of aqueous saline solution, filtered through siliceous earth and evaporated to a thick syrup in vacuo at a low temperature. The syrup is dissolved in a little water and shaken with ether. The ether removes a small quantity of a brown oil which does not have the properties of allyl-urethane or imino-carbonic acid ester. It was not examined further due to the very small quantity obtained. The aqueous liquid extracted with ether is again evaporated as completely as possible under reduced pressure and the syrupy residue is boiled for about an hour with dry acetic ester. Subsequently the weakly colored acetic ester solution is filtered and compressed to a few ccm.

Upon cooling, small, rough aggregates of crystals separate, which are transformed into colorless, fine needles with a melting point of 192° (uncorrected) by threefold recrystallization from acetic ester. The yield amounted to a maximum of 11% of the utilized sinigrin.

The compound has the composition of sinigrin less its content of potassium bisulfate. Merosingrin dissolves easily in water, alcohol and acetone, rather easily in acetic ester and chloroform, poorly in ether and benzene. It is not dissolved by ligroin. It is noteworthy that it is optically very strongly dextrorotatory in contrast to levorotatory sinigrin. Boiled with alkaline lead solution, merosingrin does not cause blackening. Fehling's solution is not changed by it; not even after lengthy boiling with diluted acids. After heating in the tube with 10% sulfuric acid for 4 hours at 120°C, no decomposition of merosingrin is noted; at 160°C destruction of the molecule by the acid occurs, accompanied by formation of humic substances and caramel odor. Since only a total of about 1.8 g of the compound was available in pure form, analyses were in part conducted by microchemical methods.

13.145 mg substance: 22.310 mg CO₂, 6.880 mg H₂O.
4.992 mg substance: 0.261 ccm N (22°C, 714 mm).
5.930 mg substance: 0.288 ccm N (21°C, 716 mm).
0.1141 g substance: 0.1038 g BaSO₄.
0.1990 g substance in 6.930 g water showed a freezing point depression of 0.230°C.

C₁₀H₁₅O₅NS. Calculated: C 45.94, H 5.79, N 5.36, S 12.28, mol. weight 261.
Found: C 46.27, H 5.86, N 5.68, 5.31, S 12.50, mol. wt. 231.

Optical determination was conducted in aqueous solution.

For sodium light, alpha at 20°C equals +8.12° (1 dm tube, concentration 5.441).

Therefore $[\alpha]_D^{20} = +149.2^\circ$

Upon treatment with acetic anhydride, merosinigrin yields an triacetyl derivative. 0.18 g merosinigrin is boiled for $\frac{1}{2}$ hour with 0.5 dehydrated sodium acetate in 5 g acetic anhydride. The mixture is poured in boiling water and, after cooling, neutralized with crystalline soda, whereby the acetyl substance separates. It is absorbed in ether. The ethereal solution is evaporated after drying over calcium chloride. A thick oil remains, which may be transformed into crystals by repeated dissolving in a little ether and very slow evaporation of the ether.

Triacetyl-merosinigrin forms large, colorless slabs with a melting point of 177°C (uncorrected).

For analysis, the compound was dried in vacuo at the temperature of water steam.

0.1230 g substance: 0.0759 g BaSO₄.

C₁₆H₂₁O₈NS. Calculated: S 8.29
Found: S 8.47.

NOTES

- (1) Paper 235, 47-82 (1897); Vol. 30, 2322 (1897).
- (2) See also the dissertation by Ludwig A. Schuetz, Jena 1914.
- (3) J. Schneider et al., Vol. 47, 1258 (1914).
- (4) Cf. also the preceding paper.